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Solar hydrogen generation from water splitting using ZnO/CuO hetero nanostructures

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Abstract

We first report a facile green strategy for in situ synthesis of CuO nanostructures on ZnO nanorods to form new ZnO-CuO hetero nanostructures by a novel method and further investigate them as photoanodes in PEC cells for solar hydrogen generation from water splitting. A high photo-to-hydrogen generation efficiency of 0.86% at the bias potential of 0.94 V is achieved.

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Keywords: ZnO/CuO hetero nanostructures; Water splitting; Hydrogen generation

1. Introduction

One-dimensional (1D) ZnO nanorods have emerged as a promising candidate for being used as photoanodes in photoelectrochemical cells (PEC) for hydrogen generation from water splitting using solar energy due to their relatively lower recombination loss and vertically aligned electrical to the charge collecting substrates [1]. However, these ZnO nanorods themselves can only utilize the light in ultraviolet region due to their wide band gap (Eg=3.2 eV, corresponding to 390 nm) which contributes less than 5% of the total energy of the solar spectrum [1-2]. To make photoanodes based on ZnO nanorods driven by visible light, the incorporation of a narrow band gap semiconductor, which can absorb the light in the visible region, has been extensively employed as a promising avenue for enhancing the PEC conversion efficiency. CuO, as a p-type semiconductor with a narrow band gap (1.2–1.9 eV), can absorb light in the visible spectrum, which is suitable for solar energy harvesting [2-3]. As a result, the combination of p-type nanoscale CuO with n-type ZnO nanorods to enhance the light absorption by matching the solar spectrum has been widely employed as a promising way to improve the PEC conversion efficiency.

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Recently, p-type CuO nanostructures have been integrated with n-type ZnO nanostructures to form p-n junctions that show interesting optical properties and find promising applications in photocatalytic hydrogen production [2, 4-5]. However, these fabrication methods normally require special apparatus, expensive raw materials, severe conditions and also time-consuming. Therefore, they have certain limitations in terms of mass production and cost effectiveness. Consequently, a facile, low-cost and scalable method is desired for fabricating ZnO-CuO p-n junctions.

In this work, we present a simple yet effective method for direct integration of CuO nanostructures with ZnO nanorods on indium tin oxide (ITO) substrates and then use them as photoanodes in PEC cells for water splitting for hydrogen generation.

2. Experiments

2.1 Synthesis of ZnO nanorods

ZnO nanorods on ITO substrates are synthesized by the galvanostatic cathodic reduction method based on our previous work [6]. The electrolyte contains 5 m mol/L $Zn(NO_3)_2$ and hexamethylenetetraamine aqueous solution. The current density is 0.25 mA/cm^2 and the temperature of electrobath is 90^{o}C.

2.2 Synthesis of ZnO/CuO hetero nanostructures

Commercially available low-cost copper foam is used as the Cu sources for synthesizing the CuO nanocrystals. After cleaning and drying at room temperature, the copper foam is put on a support and transferred into a furnace. When the copper foam is thermally heated in air, CuO nanocrystals are evaporated and then deposited over/around the ZnO nanorod arrays that are placed over the copper foam [7].

3. Results and discussion

Figures 1(a-b) show the top view and cross-sectional SEM images of the ZnO/CuO hetero nanostructures respectively, where the inset in Fig. 1(a) is a SEM image of the ZnO nanorods on an ITO substrate. It can be seen that the CuO nanostructures can be successfully integrated not only on the top surface of the ZnO nanorods, but also inside the ZnO nanorods arrays resulting in intimate contact between the p-type CuO and n-type ZnO. Figure 1(c) shows the photocurrents generated by using the ZnO/CuO hetero nanostructures as photoanodes in three-electrode photoelectrochemical cells under the illumination of one sun (AM1.5, 100 mW). The combination of p-type CuO nanostructures with n-type ZnO nanorods can significantly enhance the PEC properties. The photo-to-hydrogen generation efficiency of the ZnO/CuO hetero nanostructures as shown in Fig. 1(d) reaches a maximum value of 0.86% at the bias potential of 0.94 V, which is higher than the reported efficiency (0.71%) of CuO-core/ZnO-shell nanostructures in reference [2].

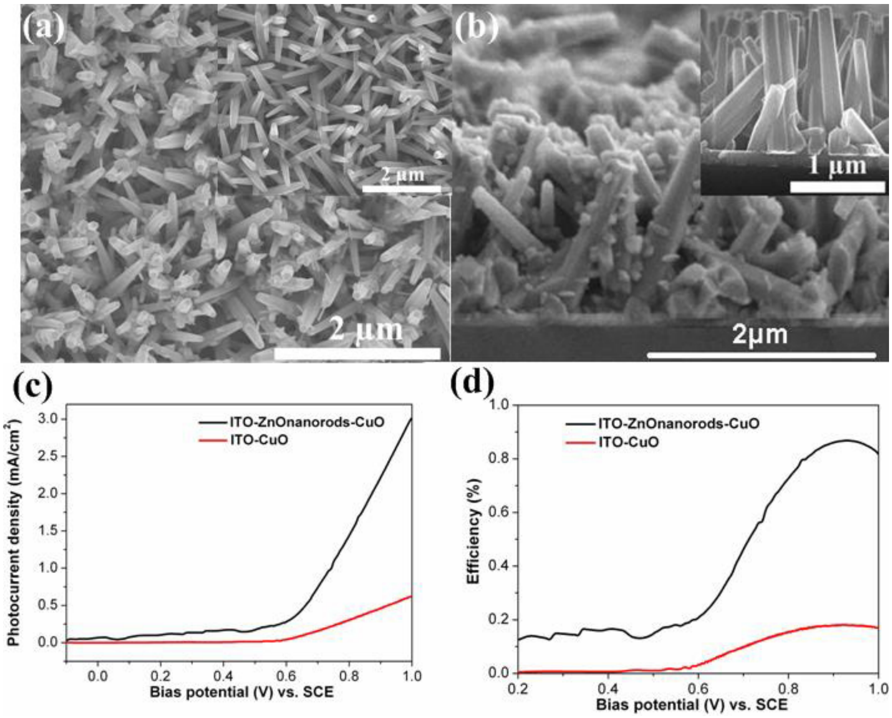

Figure 1 SEM image of the ZnO/CuO nanostructures (inset shows the ZnO nanorods): (a) top-view, (b) cross-sectional view, (c) photocurrent density versus bias potential at white light illumination of 100 mW cm^{-2}, and (d) photon-to-hydrogen generation efficiency versus bias potential at white light illumination of 100 mW cm^{-2}.

Conclusion

Novel ZnO-CuO hetero nanostructures have been successfully fabricated by a simple electrochemical method combined with a facile and cost-effective thermal oxidation. A high photo-to-hydrogen generation efficiency of 0.86% at the bias potential of 0.94 V of the resultant ZnO-CuO hetero nanostructures as photoanodes in PEC cells is achieved.

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Biography

Qiaobao Zhang obtained his M.S. degree in Electrochemistry from Xiamen University in 2010. He is now pursuing his Ph.D. degree at Department of Mechanical and Biomedical Engineering, City University of Hong Kong. His research focuses on the synthesis and application of novel metal oxide nanostructures and their composites for energy storage, including lithium ion batteries and supercapacitors.

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